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THE ANALYSIS OF ARSENIC(III) BY DIFFERENTIAL PULSE POLAROGRAPHY IN HYDROCHLORIC ACID - HYDROXYLAMINE HYDROCHLORIDE ELECTROLYTE

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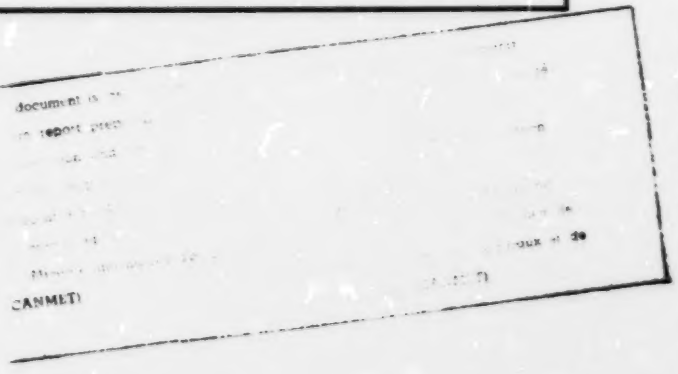

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MICROMEDIA

THE ANALYSIS OF ARSENIC(III) BY DIFFERENTIAL PULSE POLAROGRAPHY IN HYDROCHLORIC ACID - HYDROXYLAMINE HYDROCHLORIDE ELECTROLYTE

by

R.M. Morrison*

ABSTRACT

The analysis of arsenic(III) by differential pulse polarography (DPP) has been examined using saturated aqueous hydroxylamine hydrochloride as the electrolyte to overcome the deleterious effect of ferric ion on HCl electrolyte polarography. The effects of acid strength and ferric ion additions on the polarogram were investigated. The accuracy and precision of the method determined from studies of synthetic solutions and the results of analysis of samples from actual ferric ion leaching studies of niccolite are reported. Using the prescribed procedure, confident arsenic(III) analysis at the 10 ppm level in 0.3 M $FeCl_3$ - 0.3 M HCl was realized; this corresponds to an As(III):Fe(III) molar ratio of 1 to 10^7.

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ANALYSE DE L'ARSENIC III DANS UNE SOLUTION D'ACIDE CHLORYDRIQUE AU MOYEN DE LA POLAROGRAPHIE DIFFÉRENTIELLE À IMPULSION - ÉLECTROLYTE DE CHLORHYDRATE D'HYDROXYLAMINE

par

R.M. Morrison*

RÉSUMÉ

On a fait l'analyse de l'arsenic III à l'aide de la polarographie différentielle à impulsion (DPP) en utilisant une solution saturée de chlorhydrate d'hydroxylamine comme électrolyte pour surmonter l'effet délétère de l'ion ferrique sur la polarographie à électrolyte HCl. On a investigué les effets de la teneur en acide et des additions d'ions ferriques sur le polarogramme. Le présent rapport porte sur l'exactitude et la précision de la méthode qui ont été déterminées à partir d'études de solutions synthétiques ainsi que des résultats de l'analyse des échantillons utilisés pour les études qui sont effectuées présentement sur le lessivage de la nickeline au moyen d'ions ferriques. On a réalisé une analyse sûre en utilisant le procédé recommandé au taux de 10 ppm dans 0,3 M $FeCl_3$ - 0,3 M HCl, ce qui correspond à un rapport moléculaire As(III):Fe(III) de 1 à 10^7.

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INTRODUCTION

The determination of arsenic by differential pulse polarography (DPP) has been shown to be an accurate and sensitive method of analysis (1). Arsenic(III) is routinely determined at the 40 ppb to 60 ppm level in 0.3-1.0 M HCl solutions.

A problem is encountered in the analysis of arsenic(III) when a $\geq$100 fold excess of ferric ion is present (2). Apparently, the ferric ion oxidizes the mercury electrode, and this causes overloading of the measuring circuits. Although liquid-liquid extraction, ion exchange and reductillation may be reasonable pretreatment procedures (3,4), the use of a reducing electrolyte, hydroxylamine hydrochloride ($NH_2OH.HCl$), was investigated because of the relative simplicity of this method. The properties of a saturated aqueous hydroxylamine hydrochloride solution as a polarographic medium have been tabulated by Meites (5). According to this source, the electrolyte is capable of reducing ferric to ferrous and leaving the arsenic species unchanged and thus appears ideal as the answer to the problem of ferric ion interference. This report presents the experimental results of DPP with hydroxylamine hydrochloride electrolyte for analysing iron(III)-arsenic(III) solutions.

EXPERIMENTAL

Polarograms were obtained using a EG+G Princeton Applied Research Model 174A Polarographic Analyzer equipped with a Model 303 Static Mercury Drop Electrode (SMDE). Polarograms were recorded on a Hewlett-Packard Model 7004B X-Y recorder. The working electrode was the SMDE in the dropping mercury electrode mode; the counter electrode was a platinum wire. The

reference electrode was Ag/AgCl (KCl) and all potentials are reported versus the silver chloride reference electrode (E(vs Ag/AgCl) + 0.2224 = E(vs NHE)).

All chemicals used were of reagent grade unless otherwise stated. The water used was double-distilled and did not display any appreciable peaks in the range of potentials encountered in this study. The arsenic(III) standard solution was made by dissolving 1.3200 grams of arsenious oxide in a minimum quantity of 50% NaOH followed by the addition of 1.0 M hydrochloric acid to the neutral point and the addition of distilled water to make one litre of 1000 ppm As(III).

The hydroxylamine hydrochloride electrolyte, when first prepared, did not give a particularly good arsenic polarographic response. After a day or two, however, the arsenic polarogram improved. It is advised to allow the hydroxylamine hydrochloride to age if it is used alone. With the acidification scheme described later, the polarographic response was found to be unaffected by the maturity of the hydroxylamine electrolyte.

The synthetic leach solutions were prepared from the arsenic standard and 0.3 M $FeCl_3$ - 0.05 M $FeCl_2$ - 1.0 M HCl solutions. The small amount of $FeCl_2$ was added to buffer the oxidizing power of the ferric/ferrous redox couple close to its reversible potential.

Quantification of arsenic was done by the method of standard additions (6), the formula of which is:

$$C_u = \frac{i_1 \nu C_s}{(i_2 - i_1)(V+\nu) + i_1 \nu}$$

where C_u is the unknown concentration, i_1 is the peak current due to the unknown concentration, i_2 is the peak current due to the unknown concentration plus the standard addition, V is the volume prior to the standard addition, ν is the standard addition volume and C_s is the concentration of the standard addition.

The standard settings on the M174A/M303 instrumentation would be, typically: 5 mV sec^{-1} scan rate; 0.75 V scan range, 50 mV modulation amplitude; 1 second drop; -0.25 V start potential; DME drop mode; and medium drop (M303). Full scale current settings were determined to keep the display on scale.

The M174A manual recommends the most appropriate full current scale for DPP as 2 μA or less. Arsenic at 1.0 ppm gives a peak of ∿1 μA at the relevant acid levels. Therefore, since the work is mainly concerned with at most 100 ppm arsenic(III) in the starting solutions, the arsenic was diluted approximately 100 to 1. In a typical experiment, 8.0 mL of $NH_2OH.HCl$ (aq), 1.0 mL of 3.0 M HCl and 100 μL of 100 ppm As(III) - 0.3 M $FeCl_3$ would be added to the polarographic cell. As will be recounted later, the ferric ion level that is reduced in contact with $NH_2OH.HCl$ has to be taken into account when performing the analysis. For example, it was found that 100 μL of 0.3 M $FeCl_3$ (3×10^{-5} mole Fe(III)) was quickly reduced by the electrolyte described above. A greater number of moles of ferric ion was not reduced to a level which allowed interference-free polarograms to be obtained. Consequently, smaller volumes of more concentrated $FeCl_3$ solutions would have to be used to yield meaningful results.

RESULTS AND DISCUSSION

Figure 1 shows the differential pulse polarograms of 1.98 ppm arsenic(III). By analogy with the hydrochloric acid polarograms (1), the first peak (∿-0.45 V) can be assigned to the reduction of As(III) to As(0) and the second peak (∿-0.80 V) to the subsequent reduction of As(0). (The off-scale peak is a polarographic maximum). The first peak is used for quantitative analysis.

Figure 1 also shows that the peak currents and positions are dependent upon the acidity of the electrolyte. As the acidity of the medium increases, the arsenic peaks become stronger. It was also noted that the reducing power of the hydroxylamine hydrochloride medium becomes much less when the pH is lowered. Thus these two factors have to be taken into account in designing the analytical system. It was found that the best procedure was to allow the reduction of ferric ion to take place in the absence of added acid, to add the acid and then to run the polarogram.

Figure 2 shows the variation of peak potential and sensitivity with the added acid concentration. Since the sensitivity changes with acid concentration, it is necessary to keep the acid concentration constant in an analytical experiment; i.e., between the unknown and subsequent standard addition polarograms. Because the peak potential also varies with acid concentration, it seems reasonable to assume that if the peak potential is invariant between unknown and standard addition, then the acid concentration difference is small and the experiment is correct. This principle is used in this work.

Before the standard addition formula can be used successfully, it is necessary to show that the peak current is linearly proportional to the arsenic(III) in solution and that this current-concentration line has a zero intercept. Figure 3 illustrates that such a relationship does exist for this system in the range of 0-10 ppm As(III) and, thus, that the standard addition formula can be applied.

Experiments on synthetic solutions were performed to ascertain whether the arsenic(III) aliquot was 100% recovered analytically. Table 1 presents the results for 50, 20, 10 and 5 ppm As added with the 0.3 M $FeCl_3$ - 1.0 M HCl solutions. The arsenic(III) was determined in the polarographic cell at

approximately one ninetieth of this concentration. The precision of the method varies from 4% to 10-15% at lower levels. These values indicate that the method is fairly accurate (±5%) at concentrations greater than 10 ppm As(III) in the original sample or 110 ppb in the polarographic cell.

There are limits to the utility of the hydroxylamine hydrochloride electrolyte. The reducing power of the electrolyte is equal to about 100 µL of 0.3 M ferric ion. Coupling this with the lower accuracy and precision at 5 ppm As(III) in these ferric ion solutions, a lower limit of 10 ppm As(III) in 0.3 M $FeCl_3$ would be prescribed. Other methods such as the addition of solid $NH_2OH.HCl$ to the cell may increase the amount of ferric ion which could be reduced thereby permitting the determination of lower arsenic(III) levels, but initial tests in this direction were not encouraging.

The arsenic(III) is metastable in the ferric ion leach solutions. The stability of arsenic(III) in the prepared synthetic solution was monitored for a period of time to see how quickly the As(III) concentration decays. For example, a solution of 0.3 M $FeCl_3$ - 1.0 M HCl containing 100 ppm As(III) yielded the following values after the stated times: in 3 days, 88 ppm; in 7 days, 80 ppm; in 9 days, 75 ppm; in 13 days, 62 ppm and in 17 days, 55 ppm.

The hydroxylamine reduces iron(III) but not arsenic(V) as Meites (5) reported. Solutions containing 100 ppm As(V) did not give a polarographic response. In addition, As(III) polarograms did not change in the presence of As(V).

The main use of this technique is to determine arsenic(III) concentrations like those encountered in the analysis of niccolite dissolved in ferric ion (2). The end product of one leaching run gave total Fe as 18.6 g/L, ferrous ion as 460 ppm; soluble nickel as 90 ppm and soluble arsenic at 100 ppm. The

ferrous/nickel ratio is 5.35 and the nickel/arsenic ratio is 1.15. If the reaction of niccolite gives Ni(II) and As(III), these ratios should be 5.0 and 1.0, respectively. Since atomic absorption measurements can not speciate arsenic(III) and arsenic(V), the exact form of arsenic is not known although the molar ratios of the soluble species suggest that most of the arsenic is in the +3 form. With this DPP technique, the measured As(III) concentration is 57 ppm ($\pm$3%) which suggests that the arsenic(V) concentration is 43 ppm. When the equivalents of oxidation are totalled, the ratio of Fe^{2+} expected/ Fe^{2+} found is unity.

The DPP technique used here allowed the identification of the metastable As(III) species where no other direct analytical method could. Although there was indirect evidence for arsenic(III) from the total nickel, total arsenic and ferrous iron concentration measurements, the direct measurement of arsenic(III) proves that the solution composition reflects the proposed oxidation reaction of niccolite.

The utility of this method to real solutions deserves mention. In real hydrometallurgical process streams, the initial ferric ion concentration is often 1.5-2 molar. After leaching, the ferric ion concentration decreases to low levels (0-10 g/L) and the total arsenic concentration can be high. Assuming that there would be no electrochemically interfering elements present, this method would be appropriate for the end solutions. At Fe(III)/ As(III) molar ratios below and approaching unity, the hydrochloric acid method alone can be used (3). From Table I it can be gleaned that the molar ratio of As(III) to Fe(III) that can be analysed by the current method is 1 in 10^7 (10 ppm As(III) in 0.3 M Fe(III)). Further manipulation indicates that 50 ppm of As(III) can be measured confidently in 1.5 M ferric solutions. Thus this current method could be used to measure trace levels of arsenic(III) in even

strongly concentrated leach solutions. The measurement of even lower levels of arsenic(III) (e.g., 1-10 ppm) in 1.5 M ferric solutions may also be possible although the precision will not be particularly good. Other methods such as reacting the 10 ppm As(III)-1.5 M Fe(III) solution with solid NH_2.OH.HCl, and measurement with DPP polarography in HCl may extend the technique although preliminary studies on the reaction between Fe(III) and solid NH_2OH.HCl were not overly encouraging.

CONCLUSIONS

Saturated hydroxylamine hydrochloride aqueous solution has been examined as an electrolyte for polarographic studies of arsenic(III) in the presence of ferric ion. The method is suitable provided the acid concentration of the solution is constant. It was found that 92-120% As(III) recovery can be obtained from the synthetic model solutions with good precision at low trace levels (5-100 ppm As(III)) in 0.3 M $FeCl_3$ solutions. This system was used to analyse niccolite leach solutions and gave results consistent with the elemental mass balances.

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Table 1. Results of DPP from synthetic leach solutions

As(III) added (ppm)	As(III) found (ppm)	% recovery
50	49(2)	98
20	19(2)	95
10	10(1)	100
5	6(1)	120

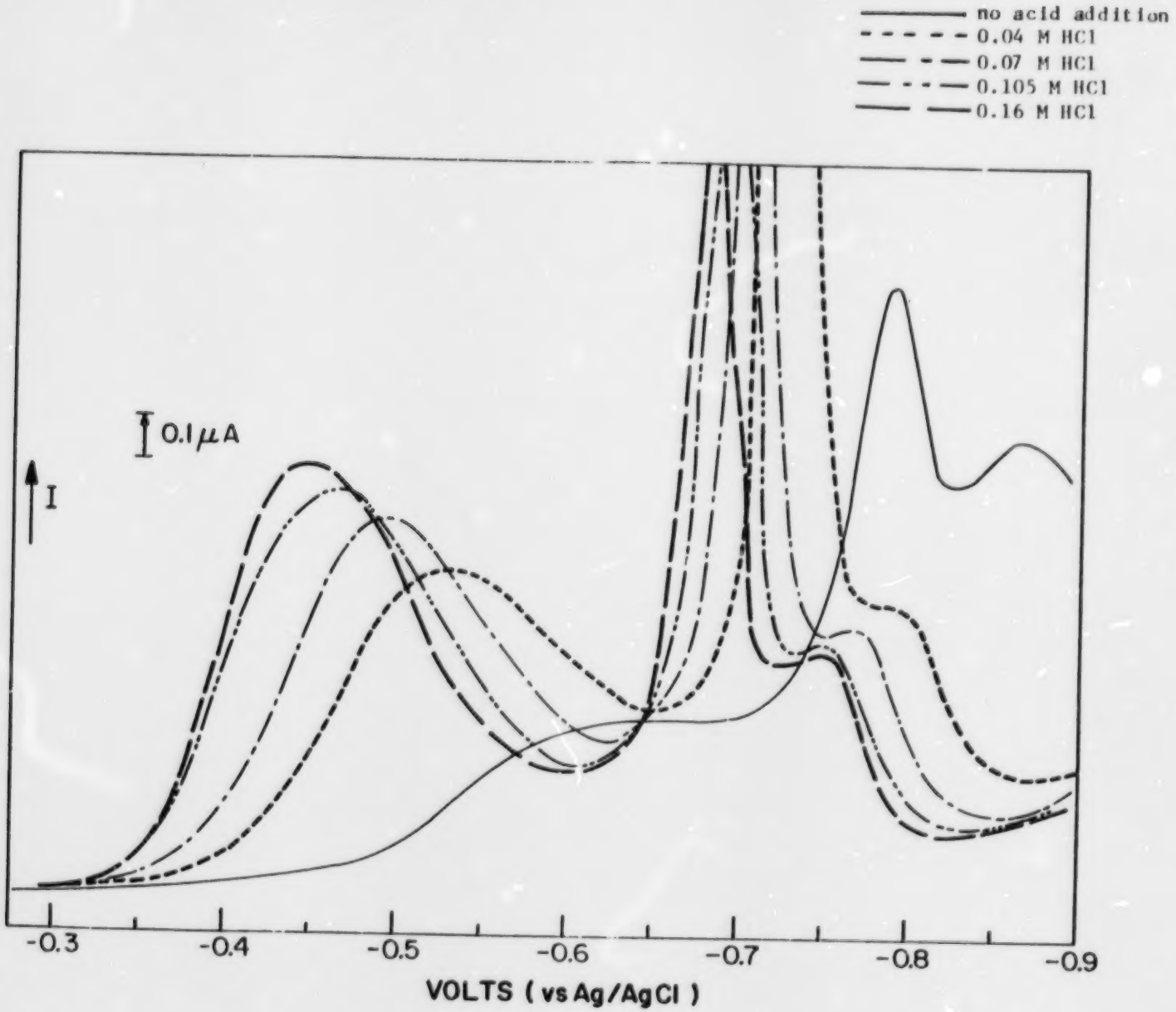

Fig. 1 - Polarograms of 1.98 ppm As(III) in saturated aqueous hydroxylamine hydrochloride electrolyte at different concentrations of hydrochloric acid.

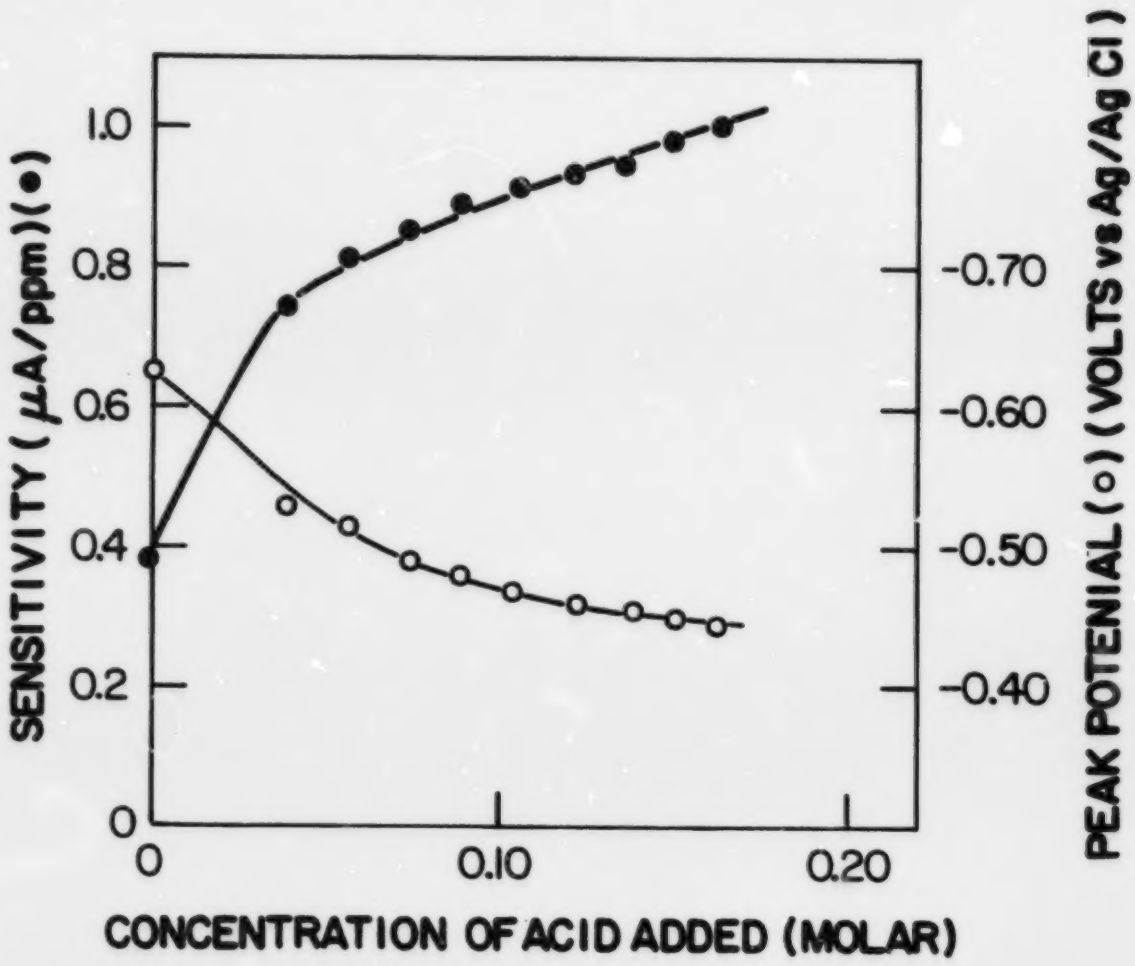

Fig. 2 - Plot of sensitivity and peak potential as a function of added hydrochloric acid.

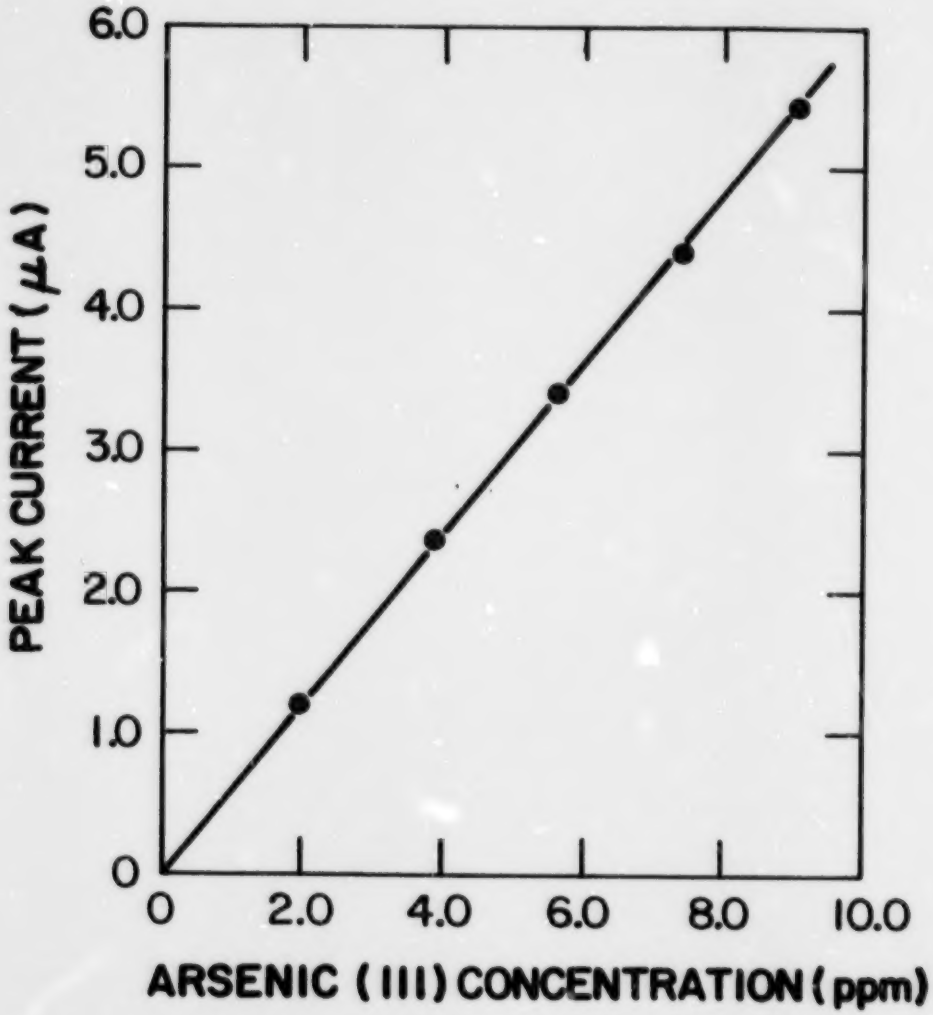

Fig. 3 - Plot of peak current (in μA) against As(III) concentration (in ppm) using saturated hydroxylamine hydrochloride - 0.09 M HCl - ueous electrolyte.